STUDIES ON FLUIDIZED BED TECHNOLOGY FOR TREATMENT OF GASEOUS POLLUTANTS: NITROGEN OXIDES (NO_X)

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By

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CERTIFICATE

This is to certify that B.Tech thesis entitled, "**Studies on Fluidized Bed Technology for Treatment of Gaseous Pollutants: Nitrogen Oxides (NO_x)**" submitted by **Rajguru Swayamjeet Rath** in partial fulfillments for the requirements of the award of Bachelor of Technology degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. He has fulfilled all the prescribed requirements and the thesis, which is based on candidate's own work, has not been submitted elsewhere.

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ABSTRACT

In a Fluidized Bed Reactor, which can be operated till a maximum of 500ºC, abatement of Oxides of Nitrogen needs to be done. The bed material chosen is manganese ore. The main fluidizing gas is compressed air and the oxides of nitrogen are fed as the secondary fluidizing fluid. The oxides of nitrogen are prepared in the laboratory itself. Along with the oxides of nitrogen, sulphur dioxide is also fed as the secondary gas for some of the experiments to check its effect on the abatement of oxides of nitrogen. Other than that temperature is also varied to see its effect. The residence time is another factor on which quality of fluidization depends hence it is also varied to check its effect on the abatement of oxides of nitrogen. Finally the characterization of the bed material before and after fluidization is done and compared to confirm the reduction in the quantity of oxides of nitrogen from what is initially fed to the Fluidized Bed Reactor.

CHAPTER 1

INTRODUCTION

Introduction

1.1 Abatement of Oxides of Nitrogen (NO_x)

There has been an enormous expansion in the emission of oxides of Nitrogen due to agricultural fertilization and industrial emissions. Nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O) are included in the oxides of Nitrogen (NO_x). Their lifespan in the atmosphere ranges from 1 to 7 days for NO and NO_2. NO_x gasses are formed whenever combustion occurs in presence of Nitrogen. Nitric Oxide is colourless, tasteless and odourless and is non-toxic, but when in contact with air it rapidly gets converted to Nitrogen Dioxide. NO_2 is a reddish brown in colour and has a pungent irritating odour. Important component of smog includes NO_2

NO_x emission contributes to the development of fine particles and ozone smog that causes illness deaths and environment problems. NO_x mainly impacts respiratory conditions causing inflammation of airways, causing irritation, coughing and pain while taking deep breaths. It can also cause inflammation, which is more like the burn caused on skin due to sun. Asthma gets aggravated and vulnerability to respiratory illness like bronchitis and pneumonia increases. Allergens response also gets aggravated by these oxides. Nitrate particles and oxides of nitrogen reduces visibility by blocking the transmission of light. Repeated exposures may also cause permanent damage or alterations in the lungs.

Also, these oxides can have adverse effects on both terrestrial and aquatic ecosystem. It contributes to smog formation. It is ground level ozone. When NO_x reacts with VOCs in presence of sunlight and heat, smog is formed. VOCs are volatile organic carbon. People who come in regular contact with this are susceptible to adverse effects such as reduction in function of lungs and lung tissue getting damaged. Vegetation may get damaged which causes the crop yield to reduce. Acid rain occurs due to the presence of these oxides in the

atmosphere. Its reaction with aerial substances forms acids, and it falls ion earth as rain, dry particles, or fog. Acid rain causes deterioration and damage of buildings, historical monuments and locomotives. Because of this water bodies becomes acidic, which makes it inhabitable for aquatic animals. The chemical balance of nutrients which is used up by animals and plants in water bodies gets upset by the presence of more nitrogen. These are also greenhouse gasses, and causes a slow rise in the temperature of earth as it gets deposited in the atmosphere along with other greenhouse gasses.

One of the newest technique for reducing the oxides of nitrogen in the atmosphere is the Fluidized Bed method. This project targets on this very technology, to abate, from the flue gas that comes out as gaseous effluents, the oxides of nitrogen.

1.2 Fluidised Bed Technology

Fluidization is a process similar to liquefaction and is the phenomenon in which solid particles get transformed into a fluid like state through suspension in a liquid or gas. The bed particles behave completely like fluids. As the thickness of the bed can be changed by changing the fluid part, objects with diverse densities similar to the bed can, by modifying either the liquid or solid fraction, be caused to sink or float. Fluidized bed is widely used in various industries. The technology of Fluidized Bed has various advantages than other methods.

1.2.1 Advantages

The advantages of having a Fluidized Bed Reactor are:

- It gives a good fluid-solid contact.
- Under isothermal operating conditions it gives a very good rate of heat and mass transfer.

- Circulation between two adjacent reactors is facilitated by the fluid like behaviour (for example regeneration combination and catalytic cracking).

- Maintenance cost is low as there is no part which moves, so the FBR is not a reactor which is agitated mechanically.

- The reactor saves space as it is mounted vertically. For a plant stationed at a place which has high land cost this aspect is particularly important.

- It is a continuous process, so can process large volumes of fluid. And it is coupled with high throughput.

- For reactions involving exothermic, heat sensitive or endothermic reactions, the fluidized bed is particularly suitable.

- Even for large scale operation, the system offers ease of control.

- It can be used as heat exchangers with low surface area in the bed due to the high heat transfer within the fluidized bed.

- Multilevel operations are also possible. So the resistance time of the fluid and the residence time of solids can be adjusted to desired levels.

1.2.2 Applications

Fluidized Bed Reactor has many industrial applications as can be seen in the above mentioned advantages. It is used in metallurgy industry, nuclear power plants, petroleum, chemical, and bio-chemical industries. Fluidized-Bed Catalytic Cracking (FCC) is widely used and important process of refinery for converting less profitable, heavy oils into more

profitable gasoline and lighter products. In Petroleum industry, it is largely used for FCC, in chemical operations like carbonization and gasification of coal, iron oxide reduction, sulhut ore's roasting, fertilizer's granulation, granular material's blending, combustion, incineration, for formation plastic with the help of rubber, in the recovery of acetone, polyethylene's formation, to convert hydrocarbons to styrenes and in pyrolysis and in physical operations i.e. solid's drying such as that of minerals that are crushed, polymers, sand, crystalline products, pharmaceuticals, and fertilizers, using plastic to coat metals and particles in agricultural and pharmaceutical industries, for solid's granulation and transportation, cooling and heating of water and in treatment of waste etc. Fluidization's commercial applications include cement clinker production, reforming, FCC, aluminium hydroxide's calcination, synthesis using Fisher-Tropsch process, regeneration of catalyst , granulation (growing particles) and drying of yeast, fluid coking, waste water treatment by bio-oxidation process, in solid's transportation like slurry pipeline for coal and in oxidation reactions involving solid catalyzed gas phase reactions.

1.3 Objective of the Work

The objective of the present work is planned as follows:

- To study the effect of various system parameters (temperature and residence time) on the abatement of the oxides of nitrogen in the Fluidized Bed Reactor.
- To analyse the bed material before and after the reaction.
- To study the effect on fluidization on passage of sulphur dioxide as the reacting gas with oxides of Nitrogen.

1.4 Thesis Layout

The thesis has five chapters.

1st Chapter: It describes the introduction to research work.

2nd Chapter: It gives the comprehensive layout of the abatement techniques used in different industries for the abatement of oxides of nitrogen (NO_x). It then talks about the selection of bed material and the details about the bed material and its uses.

3rd Chapter: This highlights the experimental set-up, materials and methods used for the abatement of oxides of nitrogen which has been prepared in the laboratory. It also gives the complete procedure of how the oxides of nitrogen and sulphur dioxide were prepared in the laboratory. This chapter also gives details about the fluidized bed reactor which was set up in the laboratory and its various components.

4th Chapter: The result obtained after the reaction are described in this chapter.

5th Chapter: The fifth chapter deals with the conclusion that have been drawn on the work done and also gives details about the scope of future work.

CHAPTER- 2

LITERATURE SURVEY

LITERATURE SURVEY

Oxides of Nitrogen are a mixture of gasses which are composed of oxygen and nitrogen. Nitric oxide (NO) and nitrogen dioxide (NO_2) are the most toxically significant compound. Oxides of nitrogen emission distribution [1].

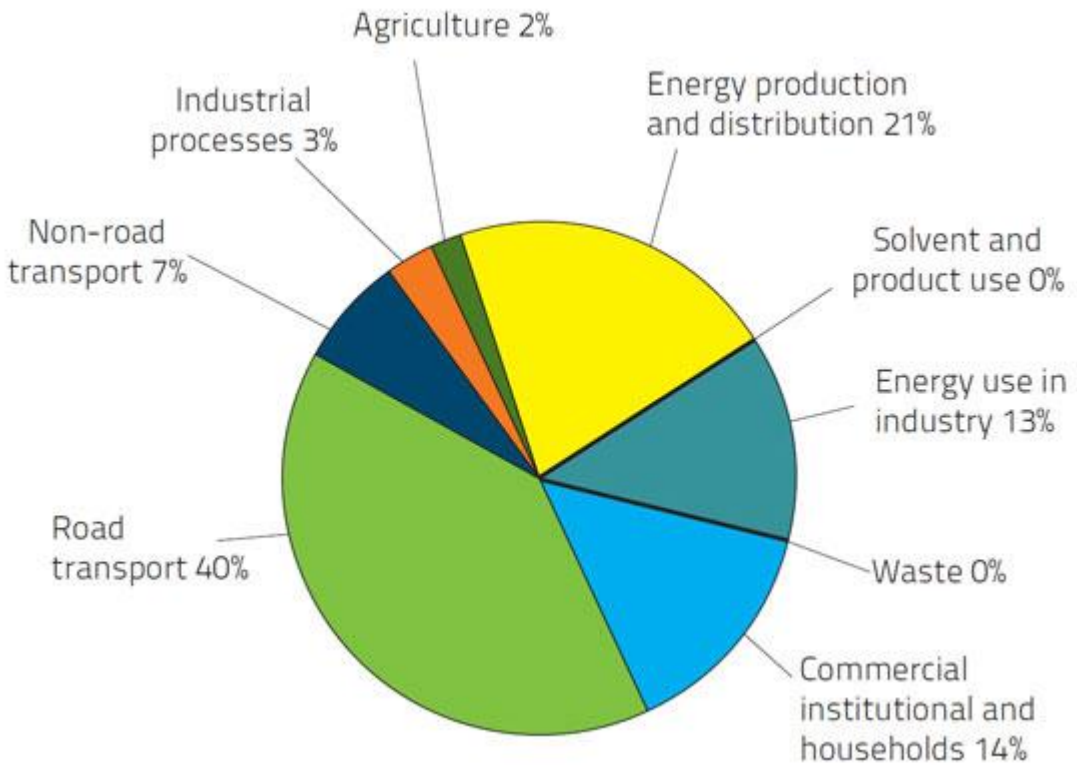


Fig 1.1 Emission Distributions of Oxides of Nitrogen (NO_x)

Researchers have developed many methods for treating the flue gas (gaseous effluents) that contains the oxides of nitrogen. None of the methods that have been found already are extremely efficient because of which the research to develop a superior method to bring down the levels of oxides of nitrogen in the atmosphere is still going on.

2.1. Different methods available for abatement of Oxides of Nitrogen (NO_x):

Various methods that are in used for abatement of oxides of Nitrogen. A summary of these methods is given below:

2.1.1. Abatement with Hydrogen peroxide: For controlling NO_x emissions several methods are there. For the treatment of NO_x, one of the most common form is gas scrubbing, with the scrubbing medium being sodium hydroxide. But it may produce waste water disposal problem as the NO_x that is absorbed is converted to nitrate and nitrite. For effective removal of NO_x scrubbing solutions containing hydrogen peroxide are used, and can give advantages not usable with sodium hydroxide. For example, to the scrubbing solution no contaminants are added by hydrogen peroxide and hence from the process commercial products can be recovered. Nitric acid is an example of such a product. Nitric oxide (NO) and nitrogen dioxide (NO_2), which are the chief components of oxides of nitrogen from any industrial sources, are scrubbed by nitric acid (35-45 wt. %) and H2O2 (0.5-1 wt. %). 0.37 lbs and 1.7 lbs of hydrogen peroxide per lb of NO_2 and NO are used. The reaction is fast when (30-80)ºC range of temperature is maintained. The reactions are:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad \text{… Eq.1}$$

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2 \quad \text{… Eq.2}$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \quad \text{… Eq.3}$$

2.1.2 Selective Catalytic Reduction: At an appropriate temperature range of (200-400) °C, this method involves the reaction of NO and NO_2 (oxides of nitrogen-NO_x) with ammonia gas (NH_3) within a catalytic bed. The species in NO_x reacts with ammonia (NH_3), and several reactions takes place. The dominant reactions are given below:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad \ldots \text{Eq.4}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad \ldots \text{Eq.5}$$

In the flue gas, NO_x mainly contains nitrogen dioxide (NO_2) although some amount of nitric oxide (NO) is also present. Ammonia is chemically adsorbed on the catalyst's active surface sites, where from the gas phase NO_x reacts. Many catalysts are available based on the temperature window. Vanadium, molybdenum oxides, titanium and tungsten, which are impregnated on ceramic or metallic substrate are the most common catalyst. TiO_2 and V_2O_5 are generally used and sometimes small amounts of heavy metals like WO_3 are added [1].

2.1.3. Selective Non-Catalytic Reduction: This process is also called thermal $DeNO_x$. In this at high temperature of (900-1000) ºC, reduction of NO_x to N_2 or takes place, in the flue gas, by reaction with urea, $(NH_2)_2CO$, and ammonia (NH_3). Since the process takes place at much higher temperature, it doesn't need any catalyst. The overall reaction is given as:-

$$H_2NCONH_2 + 2NO + \tfrac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + H_2O \quad \ldots \text{Eq.6}$$

In functional application NH3 added substance is infused into the flue gas closer to the combustion zone than in the SCR process. The effectiveness of the SNCR methodology relies on upon a few elements including the NOx level, temperature, response time, reagent-vent gas blending, and NH3/NOx proportion [1].

2.1.4. Fluidized Bed Method: Here, oxides of nitrogen existent in the flue gas are decreased by passing the gas through a suitable bed material where the oxides of nitrogen are catalytically adsorbed on the bed material. Based upon the achievement of a predetermined bed expansion the beds can be switched and the process can be conducted in parallel units connected by switching fluidized beds. For more reduction of oxides of nitrogen the process can be done in continuous operation. And hence the oxides of nitrogen can be adsorbed chemically on the surface of bed material or be reacted to form respective nitrates or nitrites.

Fluidized bed method is found to be more effective among the different methods used for the abatement of oxides of nitrogen. It is due to better solid fluid contact and also due to the numerous other benefits associated with the principle of fluidization. Solid metal particles are required to be used in the bed, in this method.

In both the chemical reaction and physical processes, gas –solid fluidized beds have been broadly utilized due to their superb gas–solid contacting and generally uniform temperature/ concentration profiles inside the beds. Gas–solid circulating fluidized beds [2, 3] find wide application in the chemical and process industries, such as fluidized catalytic cracking (FCC) [4], combustion [5], alumina calcining [6], and synthesis of fine chemicals like maleic anhydride [8]. More recently, liquid–solid circulating fluidized beds are also finding applications in the process industries such as in the synthesis of aromatic and olefinic alkylates [9, 10].

2.2. Manganese Ore as a Prospective Bed Material:

Most of the works of NO_x and SO_2 removal focuses on process either for SO_2 removal or NO_x reduction only, very few for simultaneous reductions. Techniques have been developed for simultaneous $DeSO_x/DeNO_x$ and can be categorized into 2 groups' namely: dry and wet techniques. In aqueous solution solubility of nitric oxide is low. So, chemical scrubbings, as

wet method, can't be used. In simultaneous dry removal process absorption for removal of SO_x and selective catalytic reduction for removal of NO_x is considered to be a promising process [11]. Natural Manganese Ore (NMO), which is composed of various metal oxides, mainly manganese oxide, has the potential to be used as a sorbent catalyst in the simultaneous removal of SO_x/NO_x and has good abrasion resistance. Also it is low cost and does not need any kind of pre-treatment for its operation (other than crushing). The major equation involved in adsorption of NO_2 :

$$MnO + NO_2 \rightarrow MnNO_3 \quad \ldots \text{Eq.7}$$

2.3 Utilization of Manganese Ore

The uses of NMO are (i) In the extraction of Manganese metal. (ii) Removal of Arsenic from gunpowder using low cost ferriginious manganese ore[11] (iii) Used in Chemical looping combustion- Effect of steam gasification[12] (iv)to abate fluoride from water[13]. The NMO can also be utilized for reducing NO_x and SO_x simultaneously.

2.4 Composition of NMO

A typical manganese ore contains Mn, Si, Fe, Al, Ca, Mg, Zr, and etc. The typical composition of NMO is given in table 2(a) [11]. The composition of manganese ore in different countries is given in table 2(b) [14]. The typical properties of NMO are given in table 2(c).

2.5 Material Characterization Technique

In order to understand NMO characteristics, when it is fluidized in the reactor, above the minimum fluidization velocity various samples are collected at different temperatures- room temperatures, 150ºC (423.15K), 200ºC (473.15K), 250ºC (523.15K) and 300ºC (573.15K).

The reactor takes around 1.5 hrs to reach 300ºC (573.15K). The XRD [15] pattern of the material is analysed in a 2θ range of 20º to 60º at a spanning range of 3º min^{-1}. SEM [16] and Energy Dispersive X-Ray (EDX) [17] are used to study the surface morphology and elemental composition of the samples respectively using NOVA NANO SEM 450.

Tables

Table 2(a): Typical Concentration of NMO

Component	Mn	SiO_2	Al_2O_3	Fe	CaO	MgO	Balance Oxygen of Fe and Mn
Wt %	51.83	3.13	2.51	3.86	0.11	0.25	38.31

Table 2(b): Characteristic of Manganese Ore from Different Countries

Exporting country	Weight percentage, %								P/Mn	Standard fraction, mm
	Mn	Fe	P	SiO_2	Al_2O_3	CaO	MgO	K_2O		
Ukraine	21-32	1.5-3.1	0.13-0.21	38.0-40.0	3.4-4.0	1.4-2.9	1.4-2.1	1.5-1.8	0.006	–
Ghana	30-40	1.2	0.06-0.1	10.7-18.7	2.4-2.6	4.1-4.5	3.0-3.2	0.7-1.2	0.002	6-80
Gabon	45-51	3.2-4.7	0.08-0.11	5.0-7.8	5.5-5.8	0.1-0.35	0.08-0.2	0.7-1.2	0.002	6-100
Australia	50-57	5-6	0.08-0.1	3.6-11.5	3.3-5.2	0.1-0.2	0.1-0.2	0.7-1.2	0.002	3-100
Republic of South Africa	38-51	5-16	0.02-0.04	3.0-6.5	0.3-0.9	4.0-11.0	0.3-0.6	0.02-0.1	0.0007	6-75
Brasilia	43-50	3.3-9.0	0.05-0.12	2.0-8.0	3.7-10.8	0.2-3.5	0.3-3.0	1.0-1.5	0.002	6-75
India	30-40	9.0-20	0.05-0.1	5.0-7.0	5.0-8.0	2.0-3.0	1.0-2.0	NA	0.002	6-100

Table 2(c): Physical Properties of NMO

Physical Property	Value
Density(gcm^{-3})	3.98
Surface Area(m^2g^{-1})	20
Pore Volume(cm^3g^{-1})	0.0392(5-3000Å)
Average Pore Diameter(Å)	134.36

CHAPTER 3

EXPERIMENTATION

EXPERIMENTATION

The manganese ore which was brought from a local supplier. First the NMO brought are to be reduced to the particle size which can be fluidized. Then the preliminary experiments are carried out using a Perspex column which has the same dimension inside which the actual reaction is intended to take place (Fig 3.1). The minimum fluidization velocity obtained at a particular flow rate is noted. Hence we now can carry the experiment in the actual fluidized bed at a much higher temperature, using the min fluidization velocity in the Perspex column. In the laboratory a stainless steel made Fluidized Bed Reactor has been designed. NMO of definite size is selected as bed material and the change which occurs at the high temperatures are studied. After that two sets of experiments were carried out where the laboratory prepared nitric oxide and nitrogen dioxide were allowed to mix with the fluidizing gas there by fluidizing the bed material. In the first case only oxides of nitrogen (with ammonia as catalyst) are used as the fluidizing gas whereas in the second case oxides of sulphur (Sulphur Dioxide-SO_2) is also mixed. (SO_2 is also prepared in the laboratory). The bed materials are fluidized using a compressor.

3.1 Experimental Set-Up

The different components of the experimental set-up is shown by Fig 3.2(a-h) and schematic diagram of the experimental set-up is shown in Fig 3.3. The compressor at a maximum pressure of 2 kg is used to fluidize the bed material. The reactor and the pipes used to build up the FBR is made up of Stainless Steel 316 grade and is fabricated with the help of Mechmomine Kolkata and is able to withstand pressures till 5 atm (506625 Pa). The length of the reactor column in 20.5” (0.5207m) and the internal diameter is 4” (0.1016m) with 0.39” (0.009906 m) thickness. The reactor is bounded in both the sides with cones of 4” (0.1016m) height and 4” (0.1016m) internal diameter, the thickness being same as the reactor column.

The removable bolt joint between the cones and the reactor column is provided with iron heat gaskets to prevent leakage. A ceramic heater is connected to the periphery of the FBR which is capable of heating the FBR to a maximum temperature of 500^0C (773.15 K). The bases of the cones are provided with wired meshes of size approximately 40 microns (40x10-6m). This wired mesh acts as the gas distributor in order to fluidize the bed materials. The reactor is also provided with two gate valves and one globe valve. The globe valve is used to maintain the air flow rate from the compressor. Beyond the globe valve there is a Rotameter to measure the flow rate of the incoming air, which would fluidize the bed material. The gate valves are used to either allow the gas to circulate or stop it at certain points.

3.2 Materials and Methods

3.2.1. Characterization of Bed Material

The bed material, which is the NMO, is obtained from a local supplier. The gasses (NO_x with ammonia as catalyst and SO_2) were prepared in the laboratory.

Air is used as the primary fluidizing medium for the experiment whereas the prepared gasses are used as secondary gas. The air flow is maintained using a compressor and its flow rate is measured using a rotameter.

The NMO sample is analyzed for knowing about different components present in it. After experiments the bed materials are also analyzed to confirm the results. The various elements present before and after the experiments are compared, and from these comparisons we can say that the reaction has taken place, due to which the composition have changed.

Bed material, which acts as one of the reactants, is of great importance without which the FBR cannot be designed. NMO with an average particle size of 360 microns is used. The small particle size provides adequate fluidization for NMO bed and more surface area for adsorption of the oxides of nitrogen.

3.2.2 Material Preparation

The NMO which was brought in form of large stones needs to be made to powdered form for it to be used as a bed material for fluidization process. Other than the particle size, density plays the major role in deciding the fluidization characteristic. Hence the density of the NMO was first calculated. The density was calculated by water displacement method. The procedure is as follows:

- Beaker was filled with water up to its brim.
- The amount of solid was weighed before immersing in the liquid.
- Solid was then put inside the beaker.
- The displaced water was collected in a tray.
- The displaced liquid was taken in a measuring cylinder to measure its volume
- Density was then calculated by: Density = Mass/Volume.

The density calculation observation are given in table 3(a). The average value of density comes to be 3.384 $gm.cm^{-3}$. Now since the density comes to be 3.384 $gm.cm^{-3}$- it can be a Geldart B or Geldart D particle. Since Geldart D particle are not suitable for fluidization (it may cause spouting, unequal mixing etc.), we need to make the bed material a Geldart B particle. The size should be between 40 to 500 microns.

The reduction of size takes place in two steps:

1. Crushing- The solid manganese ore which is in the form of large stones are crushed initially to make it smaller so that it can be grinded to make it a powder. The crusher used is Jaw crusher.
2. Grinding- The reduced size of the particles needs to be grinded to get to the required size (40-500 microns). A ball mill was used for this purpose. In each run 30 balls of equal size are used and ball mill is run for 30 to 40 minutes in a single run. The repeated runs brought the size of the particles to required size range.

The powdered material obtained is then sieved to get the exact size range. A sieve-shaker is used for separating the particles according to their mesh sizes. It was observed that the maximum amount of particles were found in the range of 220 to 500 microns. So this size of particle is taken for the fluidization purpose.

3.2.3 Voidage Calculation and Calculation of Min Fluidization Velocity

For calculating the min. fluidization velocity from theory as well from the experimental set-up. Although the value calculated from experimental set up is to be used it will be useful to compare the results when we calculate theoretically. To calculate theoretically we need to have the value of voidage. The procedure for calculation of voidage is:

- Weigh a mass of bed material
- Put that mass of bed material inside the fluidized bed and calculate its volume.
- From the equation mass = actual vol x density we can calculate the voidage

The observations and results are given in table 3(b).

From table 3(b) the value of voidage comes out to be 0.619. Now from Ergun's equation min. fluidization velocity comes to be 0.057 m/s.

3.2.4 Preparation of Gasses

The gasses used in the experiments are nitric oxide (NO), ammonia as catalyst (NH_3) and sulphur dioxide (SO_2). The experimental set-up is given in Fig 3.4. The preparation technique for all three are given below:

3.2.4.1. Preparation of Nitric Oxide

Nitric Oxide is readily oxidized to Nitrogen dioxide when it comes in contact with air. This experiment was conducted in a well-ventilated area. The procedure for the process is

- Dilute ferrous sulphate solution was put in a round bottom flask.
- This solution was then acidified using dil sulphuric acid.
- The above solution was well mixed.

- Conc Sodium Nitrite solution was then added and on adding the solution turns dark brown due to the formation of nitroso ferrous sulphate.
- It was then heated in an electrical heater.
- This nitroso ferrous sulphate on heating produces nitric oxide which was collected in bladder. (Fig 3.5)

The overall equation for the above process is:

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe\ (SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO \quad \ldots \text{Eq. 8}$$

3.2.4.2. Preparation of Sulphur Dioxide

Copper turnings when heated with conc sulphuric acid gives out sulphur dioxide. The procedure for the process is:

- A known and weighed amount of copper turning was put in a round bottom flask.
- Conc sulphuric acid was then added to it.
- Heat was supplied through an electric heater.
- The produced SO_2 was collected in a bladder through the upward displacement of air.
- The bladder was secured using a pinch cork. (Fig 3.5)

3.2.5. Methods:

First the NMO was fluidized for 2 hours in the Perspex column to remove the easily breakable part to prevent the change in average particle size. In the Perspex (Fig 3.2) column preliminary experiments were carried out to understand the bed behavior when the bed was allowed to fluidize with atmospheric air. Depending on the observations from Perspex column experiments, same amount of NMO is then fed into the Stainless Steel column to study the effect of temperatures when the NMO was allowed to fluidize. Various characterization were also carried out on the NMO to support it. Depending on the results obtained, two more experiments were carried out where the oxides of nitrogen (with

ammonia as the catalyst), in the first case, and sulphur dioxide (along with NO_x and ammonia as the catalyst), in the second case was used as the secondary gas.

In the first experiment 500 grams of NMO ($320x10^{-6}$) was fluidized with a mixture of air and NO produced in the laboratory. Ammonia was also added with NO and is used as a catalyst in the reaction. The air was supplied by the compressor and NO and NH_3 were supplied through gas bladder. In the bladder the prepared gasses from the laboratory were stored. The bed was allowed to run at 200°C with a residence time of 30 minutes. The bed material was collected after 30 minutes and characterization was done. The temperature was then increased to 300ºC and a residence time was fixed at 30 minutes. The bed material was then collected and characterization was again done.

In the second experiment 500 grams of NMO ($320x10^{-6}$) was fluidized with a mixture of air, NO with ammonia as catalyst and sulphur dioxide (SO_2). SO_2 was also supplied in gas bladder, prepared from the laboratory. The bed material was collected after a residence time of 15, 30 and 45 minutes. After that the characterization of the bed material was done. The similar procedure as the first experiment was carried out.

TABLES

Table No 3(a): Density Calculation of NMO.

RUN NO	**WEIGHT OF THE ORE (gm)**	**VOLUME DISPLACED (ml)**	**DENSITY ($gm.cm^{-3}$)**	**AVERAGE DENSITY ($gm.cm^{-3}$)**
1.	250.410	74	3.384	3.36
2.	300.02	88	3.41	
3.	275.56	82	3.36	

Table No. 3(b): Voidage Calculation of bed material

Mass Taken (m) (gm)	Circumference of FBR = 2 x 3.14 x r (cm)	Radius of FBR (r) (cm)	Height of fluidized bed (cm)	Area of Cross Section (A)=3.14 x r^2 (cm^2)	Density (gm/cm^3)	Voidage = 1-(m/A x h x D)
500	31.25	4.97	5	77.71	3.384	0.619

Figures

(a)Non-Fluidized State

(b) Fluidized State

Fig. 3.1 Perspex Fluidized Bed

(a) Front View of the Reactor Column

(b) Top View of the Reactor Column

(c) Top view of the cone

(d) Front view of the cone

(e) Front view of the Tubular Heater

(f) PID Controller

(g) Compressor

(h) Experimental Set-up

Fig 3.2 Different Parts of the Fluidized Bed reactor

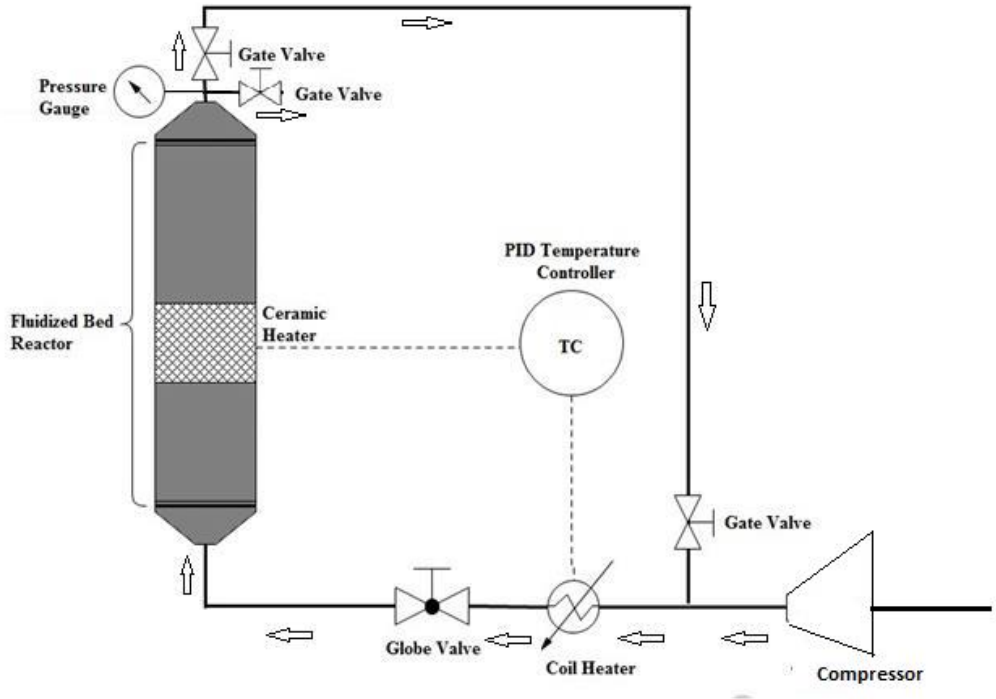


Fig 3.3 Schematic Diagram of the Experimental Set Up

(a)At the start of the reaction

(b) After some time

Fig 3.4 Experimental Set-up for the Production of NO and SO_2

Fig 3.5 Gas Bladder containing NO

CHAPTER 4

OBSERVATION AND RESULTS

OBSERVATION AND RESULT

4.1 Analysis for Manganese Ore as bed material with or without flue gas treatment.

Preliminary study regarding the bed material and its characterization is very important to carry out the experiment. As literature indicates the oxides of nitrogen will get adsorbed with the metal particles at high temperature, it is essential to know the characteristic of NMO at different temperatures for the present work. Depending on the results obtained from preliminary characterization of NMO, the further reactions in the fluidized bed are carried out accordingly.

4.1.1 Fluidization Parameter

Fluidization is one of the best methods of providing proper fluid-solid contact. Different aspects affect the quality of fluidization. Again many aspects are to be analyzed as prerequisites for proper fluidization. Minimum fluidization velocity is one of the aspects which is to be determined first. Preliminary experiments suggests that NMO particles of 320 microns size have good fluidization quality and is used as a bed material for the reaction. The theoretical value of the minimum fluidization velocity comes to be 0.057 m/s. From the experimental data for finding min fluidization velocity (Table 4(a)) a graph was plotted between ΔP (Kpa) and u (m/s) –Fig 4.1 and the minimum fluidization velocity was found to be 0.085 m/s. It is almost same as the theoretical value.

4.1.2. Heating Process

Fig 4.2 indicates the time taken by the FBR to reach the maximum temperature of 500^0C (773.15K). The reactor takes almost 42 minutes to attain a temperature of 200^0C (473.15K), 58 minutes to reach 250^0C (523.15K) and 93 minutes to reach 300^0C (573.15K).

4.1.3 XRD Analysis

Various researchers have studied the phase characterization and elemental analysis of NMO but the data analysis for the composition of NMO are found to be non-uniform because of its variation in elemental composition at different places. The XRD patterns of NMO are observed and are shown in Fig 4.3. The major components at room temperature are manganese (Mn), Manganese Oxide (MnO_2), silicon dioxide (SiO_2), Calcium Oxide (CaO), Iron (Fe), Aluminium Oxide (Al_2O_3), and Magnesium Oxide (MgO). The XRD pattern of the elements are referred form JCPDS file of X'Pert HighScore software. Using peak broadening technique of X'Pert High Score software for XRD analysis, one can clearly differentiate the peaks. The Peaks of Mn are coming at around 28.68º, 37.33º and 56.65º. There are no traces of any Manganese nitrate from the XRD analysis.

After the reaction has taken place the bed material was again analyzed. First, the analysis was done after 15 minutes at a temperature of 200ºC. The gasses passed are nitric oxide, ammonia and sulphur dioxide. There are peaks for Manganese Nitrate found which proves that NO is being absorbed (Fig 4.4a). The bed material was again analyzed after 30 minutes (Fig 4.4b) and 45 minutes (Fig 4.4c). The peaks for the nitrate and sulphate are both found in all the three cases. Next the analysis was done after passing only nitric oxide and ammonia with the fluidizing gas. This time the residence time was taken to be 30 minutes. Here also a peak for manganese nitrate was found (Fig 4.5a). The temperature was then increased to 300ºC. The residence time was taken to be 30 minutes again (Fig 4.5b). Again only nitric oxide and ammonia were passed and SO_2 was not passed. The peak for manganese nitrate was again found. Hence we can be sure that the nitric oxide was adsorbed on the surface of Manganese ore.

4.1.4 SEM and EDX Analysis

To analyze the morphological structure of the sample SEM is done. The SEM images of NMO before and after the reaction are given in Fig 4.6(a-c). The EDX analysis gives the idea about the composition of different elements in the bed material. As expected we do not see any sulphur or nitrogen present. Oxygen is present in the highest quantity, followed by Manganese (table 4(b)). The graph of the different concentration of bed material is also given (Fig 4.7).

SEM of the particle after the experiments are carried out are also done. The EDX results for the first experiment (at 200ºC and 300ºC) are also plotted in Fig 4.7 and its respective elemental analysis in tabular form is given in table 4(c). Similarly for the second experiment for all the residence time the EDX results are plotted in Fig 4.8 and elemental analysis is done in table 4(d).

Tables

Table No 4(a): Experimental Values for Calculation of Min Fluidization Velocity

Sl.No.	H1(mm)	H2(mm)	ΔH(mm)	ΔP (Kpa)	Flowrate (LPM)	Velocity (m/s)
1.	193.5	193.5	0	0	0	0
2.	190.6	196.4	5.8	0.75	10	0.021
3.	183.8	203.2	19.4	2.5	20	0.043
4.	179.5	207.5	28	3.63	30	0.064
5.	174.5	212.5	37.5	4.85	39	0.083
6.	175	212	37	4.79	40	0.085
7.	175	212	37	4.79	45	0.096
8.	175	212	37	4.79	50	0.11
9.	175	212	37	4.79	55	0.18

Table No 4(b): EDX Analysis of NMO

Element	**Weight %**	**Atomic %**
O K	45.24	72.42
Mn K	2.36	2.15
Fe K	0.19	0.65
Ca K	11.95	7.64
Si K	28.68	13.37
Mg K	5.71	2.62
Zr L	5.88	1.65

Table No 4(c): EDX Analysis after reaction at 200°C (only NO and NH_3).

Element	Weight %	Atomic %
O K	45.24	72.42
Mn K	2.36	2.15
Fe K	0.19	0.15
Ca K	11.95	7.64
Si K	28.68	13.37
N K	4.23	2.23
Zr L	5.88	1.65

Table No 4(d): EDX Analysis after reaction at 200°C (NO + NH_3 + SO_2) after 15 minutes.

Element	Weight %	Atomic %
O K	43.00	52.04
Mn K	25.10	25.87
Si K	21.07	19.02
Al K	0.14	0.07
N K	0.41	0.21
S K	0.04	0.02
K K	0.12	0.05
Ca K	2.46	0.89
Mg K	5.24	1.38
Fe K	1.23	0.32
Zr L	0.88	0.14

FIGURES

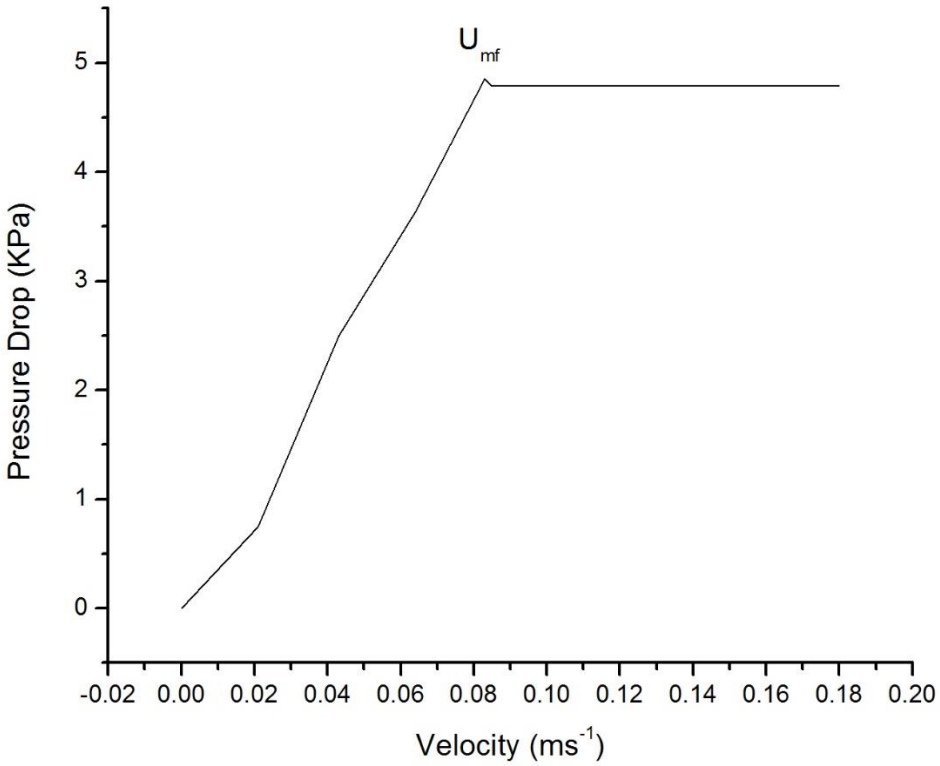


Fig 4.1 Pressure Drop Vs Velocity Plot for Bed Material (Manganese Ore) of 320 microns

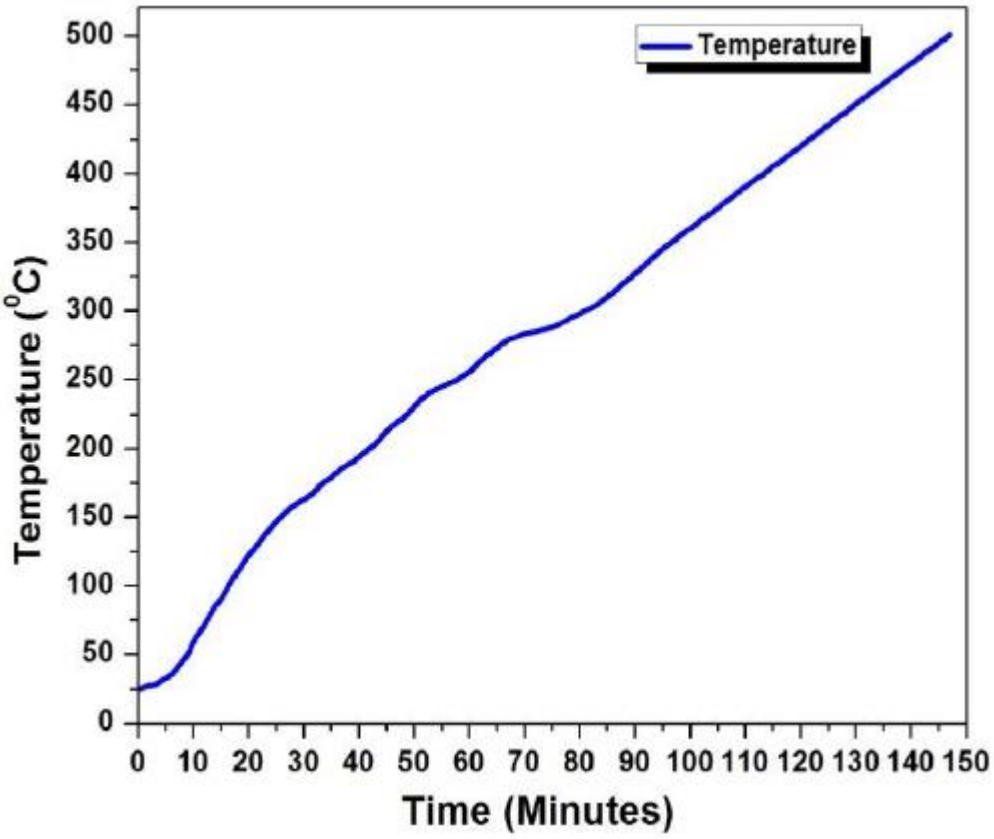


Fig 4.2 Heating Curve of Manganese Ore.

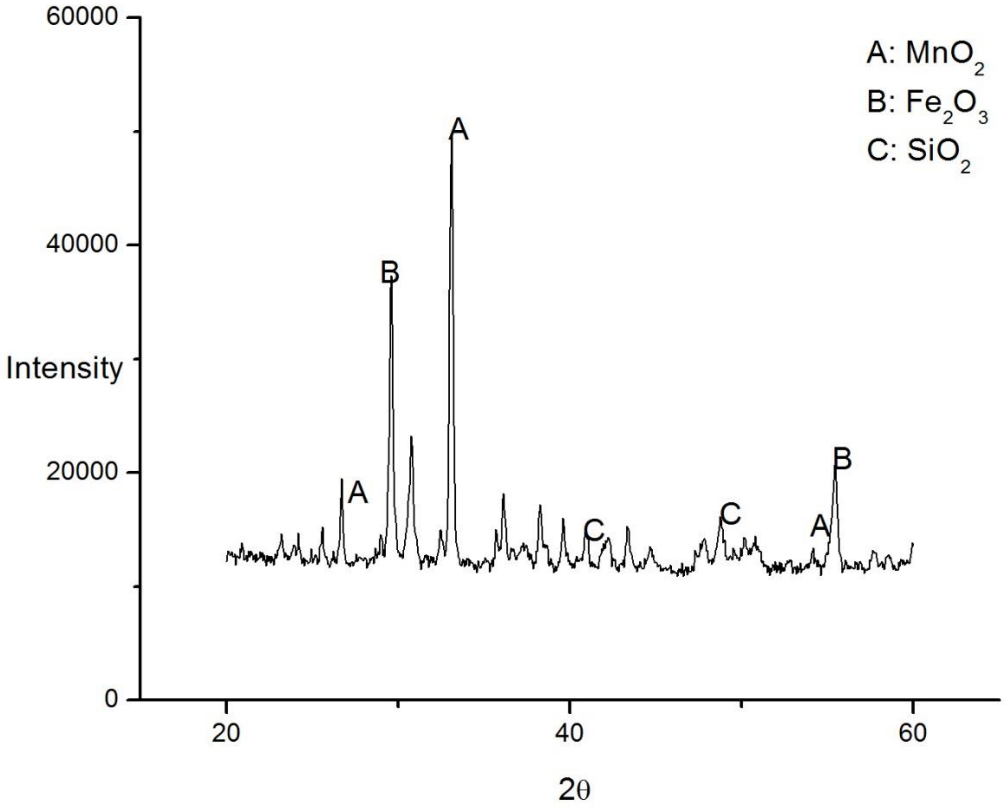
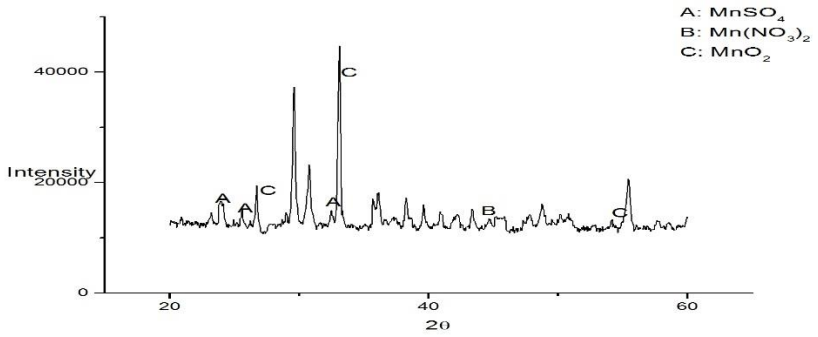
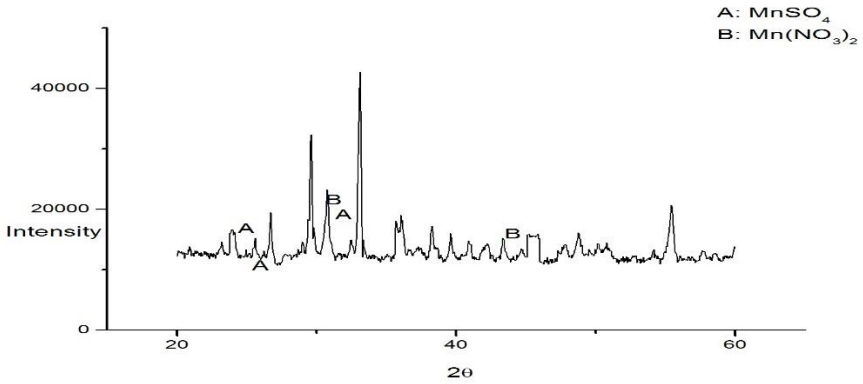


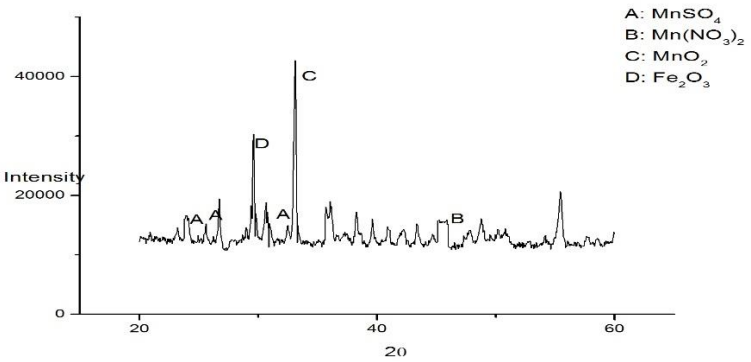
Fig 4.3 XRD Analysis of Natural Manganese Ore.



(a) After 15 Minutes.

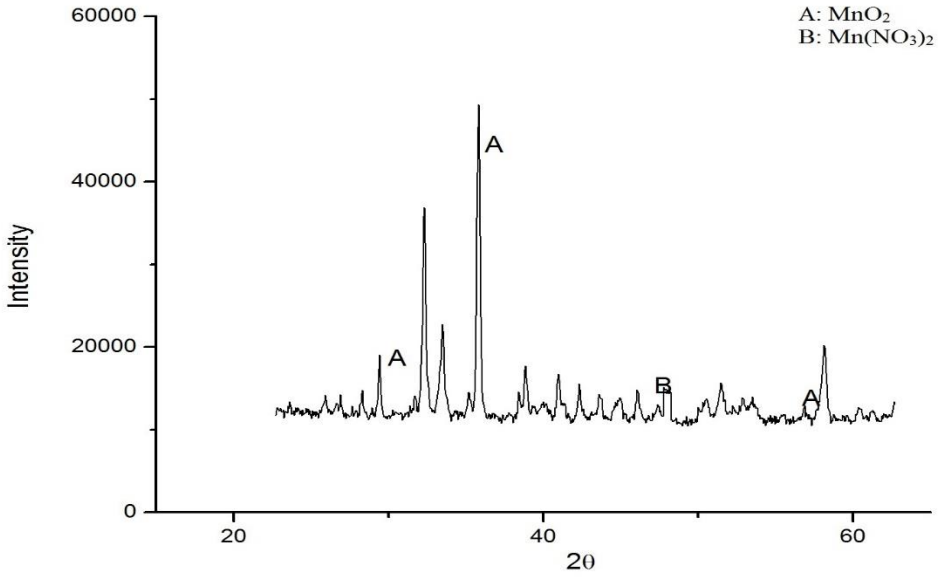


(b) After 30 minutes.

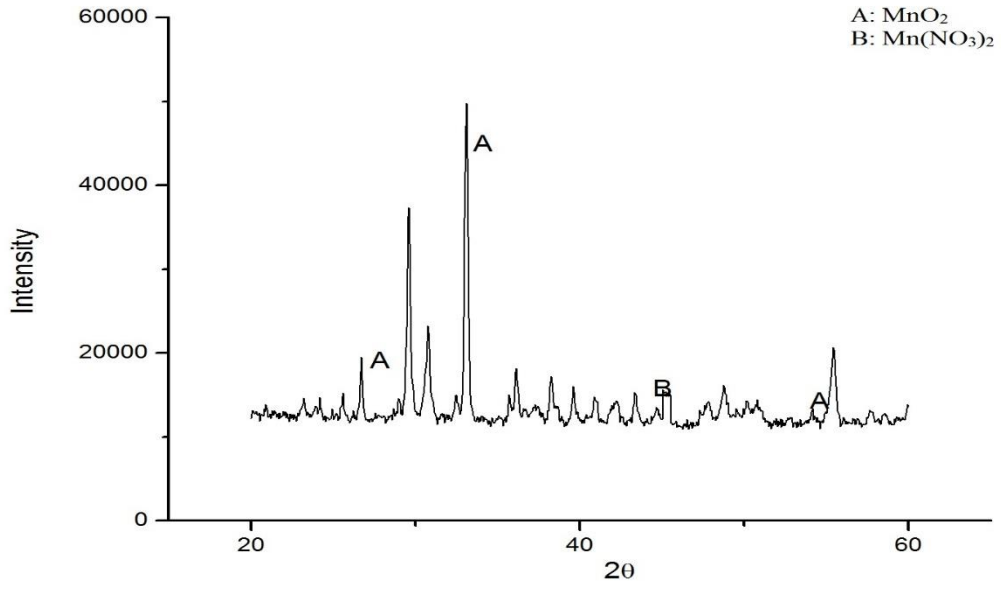


(c)After 45 minutes

Fig 4.4 XRD Analysis graph for fluidized bed after reaction with NO and SO_2

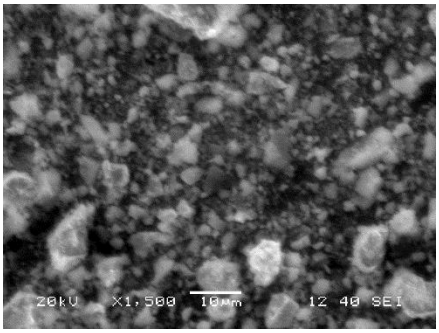


(a) At 200ºC

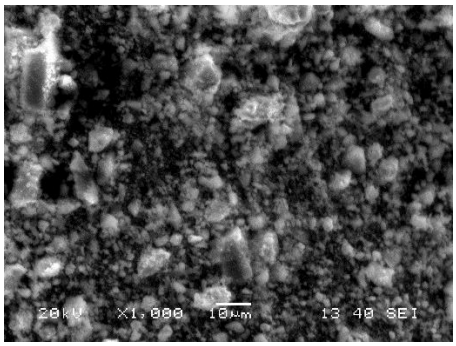


(b) At 300ºC

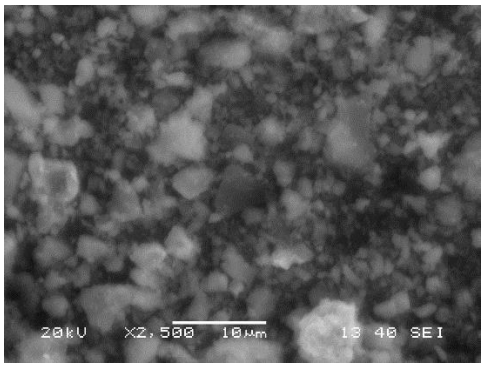
Fig 4.5 XRD Analysis of Bed Material after reaction with only NO



(a) At magnification 1000



(b) At magnification 2500



(c) At magnification 5000

Fig 4.6 SEM Images for Manganese Ore

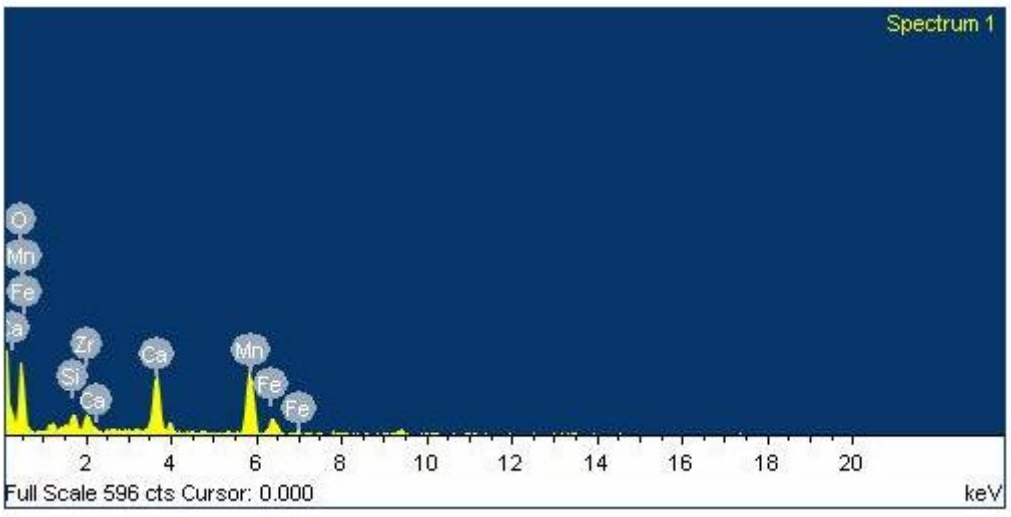
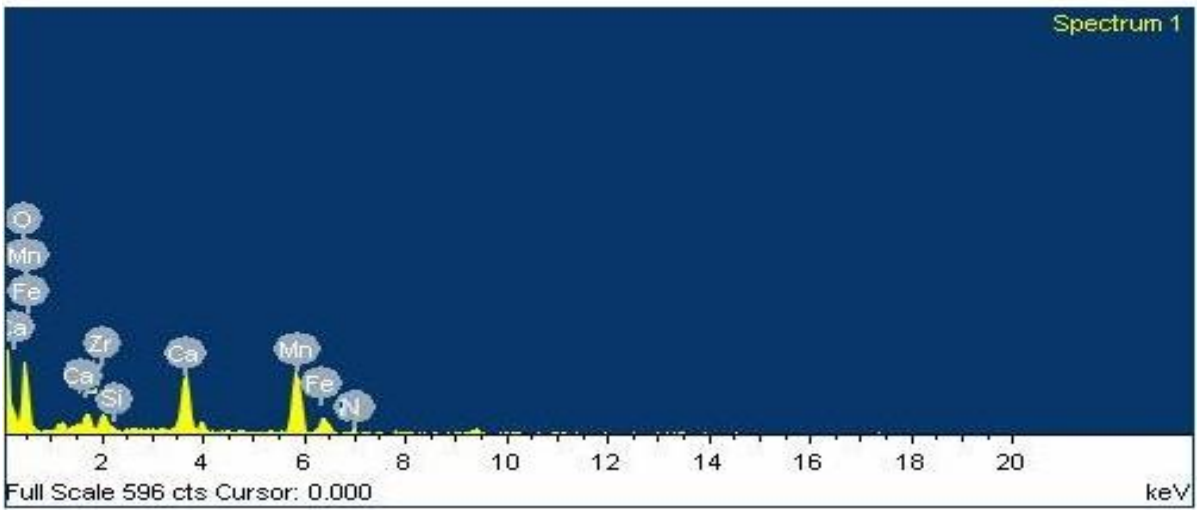
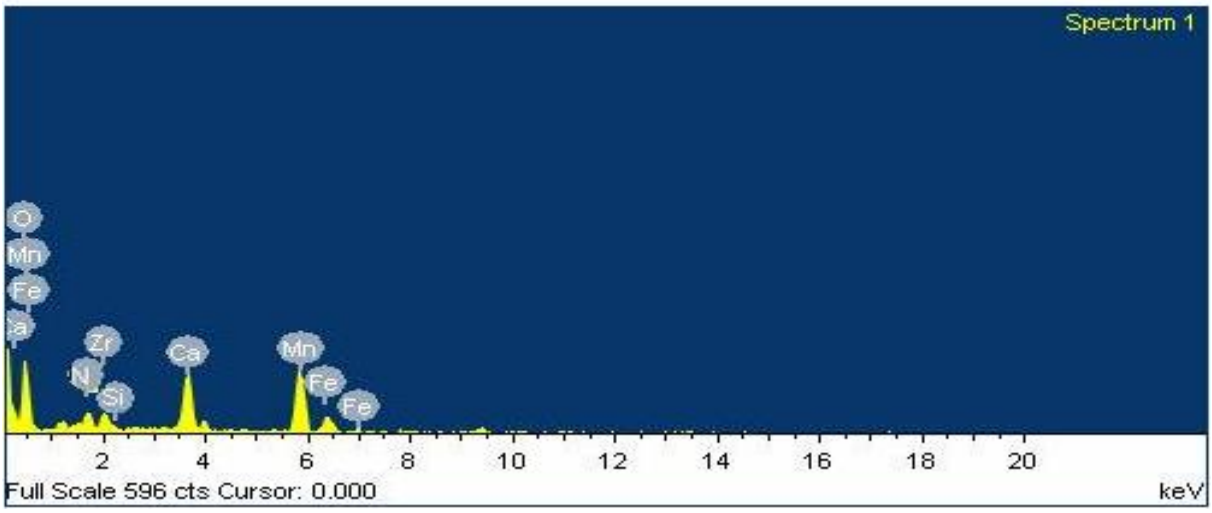


Fig 4.7 EDX Analysis of Natural Manganese Ore

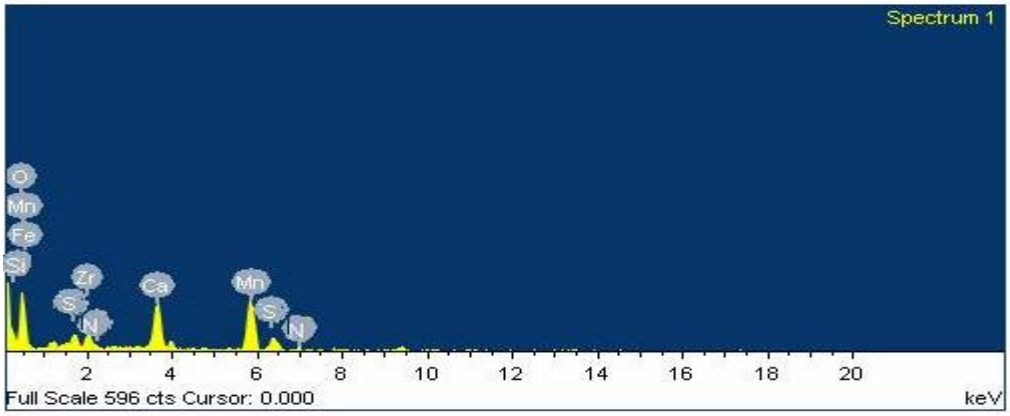


(a) At 200ºC

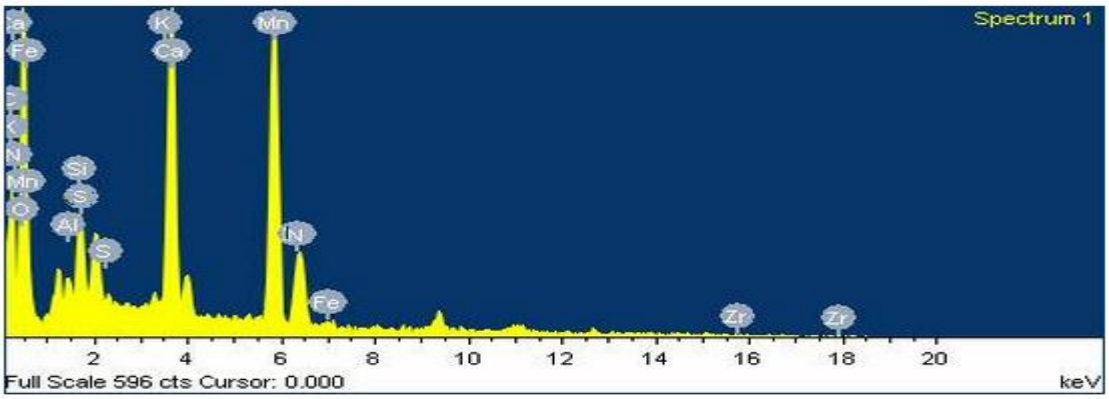


(b) At 300ºC

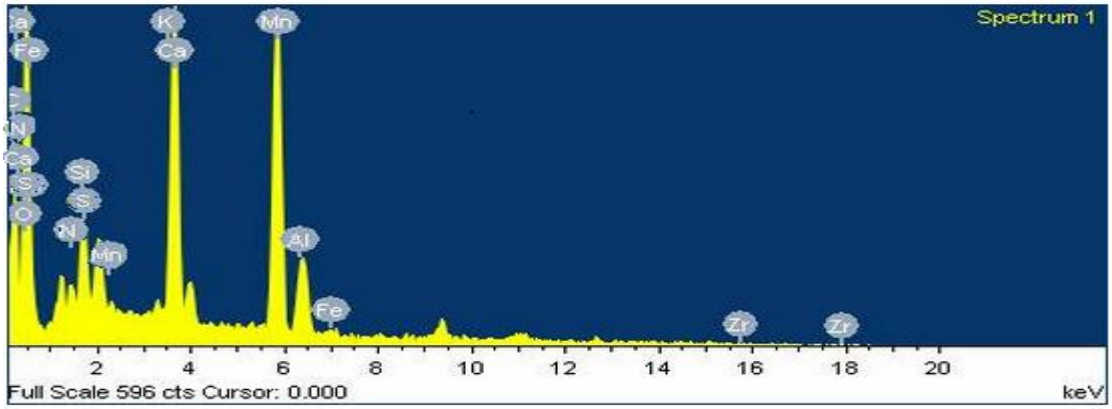
Fig 4.8 EDX Analysis after fluidization with NO only



(a) After 15 Minutes



(b) After 30 Minutes



(c) After 45 minutes.

Fig 4.9 EDX Analysis after Reaction with NO And SO_2 at 200ºC

Chapter 5

Conclusion

Conclusion

5.1 Conclusion

Two sets of experiments were carried out. One with nitric oxide (NO) and (NH_3) are mixed with fluidizing gas (compressed air). This experiment was carried out at two temperature condition-one at 200ºC and other one at 300ºC. From the XRD analysis we can confirm the formation of Manganese Nitrate which forms due to the chemical adsorption of NO_2 on MnO_2. Here NH_3 acts as a catalyst and does not take part in the reaction. Although exact concentration of Manganese Nitrate could not be determined but through EDX analysis it was found that for the same residence time (30 minutes) concentration of Nitrogen element in the bed is more. Hence on increase of temperature the chemical adsorption of oxides of nitrogen increases. Also beyond 300ºC, from theory we know that ammonia decomposes, hence above 300ºC experiments were not carried out.

In the second set of experiments, sulphur dioxide was also passed along with the oxides of nitrogen and ammonia. From the XRD it showed that manganese nitrate was still being formed, hence the adsorption of NO on the surface of the ore was still taking place. From the EDX analysis for 30 minutes residence time it was seen the amount of nitrogen content was more in this case. It implies that more amount of NO is adsorbed in presence of SO_2. This might be due to the fact that it is acidic in nature and promotes the adsorption of NO on the surface of the ore. Now if we compare the nitrogen concentration for different residence time we find that from 15 minutes to 30 minutes the nitrogen concentration increases rapidly. But from 30 minutes to 45 minutes there is no rapid increase of concentration of nitrogen. This might be due to the fact that SO_2 is also adsorbed on the surface of the ore and it forms sulphates. These sulphates reduces the pore size, hence reducing surface area. With decrease in surface area NO adsorption also decreases.

Hence this process can be easily used in industries as it helps in the reduction of two harmful gasses and scale up of the reactor can be done.

5.2 Scope and Future Work

- To study the usage of bed materials. The bed material, if converted to something useful, can become a boon for the industries.
- By sampling the gas exact results can be achieved.
- To study the various kinetics occurring in FBR leading to a better understanding and control of reactors
- Making the process more effective by minimizing leakage and by providing proper insulation.

ABBREVIATIONS:

FBR**:**	Fluidized Bed Reactor
NMO:	Natural Manganese Ore
XRD:	X-Ray Diffraction
SEM:	Scanning Electron Microscope
EDX:	Energy Dispersive X-Ray

REFERENCES

1. Nitrogen Oxides | NOx Abatement | H2O2 | H2O2.com – USPeroxide

2. Radojevic, M. "Reduction of Nitrogen Oxide in Flue Gasses" Elsevier, 102, 686, 1998.

3. Reh, L. and Basu, P. ŽEd. "Circulating Fluidized Bed Technology." Pergamon, New York.105, 543, 1986;

4. Ensgtrom, F.; Lee,Y.Y.; Basu, P.; Horio, M. and Hasatani, M. ŽEds, "Circulating Fluidized Bed Technology III". Pergamon, NY. 15, 182, 1991.

5. Metso Automation Inc. Application report on Fluid Catalytic Cracking Unit, 2721/07/01, 2011.

6. Joris, K.; Martin, J. and André F. "Development of fluidized bed combustion—An overview of trends, performance and cost." 76, 102, 2007;

7. Heath, T.; Jukkola, W; Lewis, R.; Malabre, L. and Smith D. "Process of calcining alumina trihydrate in fluidized bed." US Patent No.# 2799558 A; 1957

8. Renshui L. "V-P-Si composite oxide catalyst precursor used for producing maleic anhydride from butance." US Patent No # 7547655 B2; 2009.

9. Vipin, V.; Paul,S. and Cottrell, L. "Process for the production of alkylaromatic hydrocarbons using solid catalysts." US Patent No.# 5012021 A; 1991.

10. Dennis, J.; Rear, O.; Steven, S.; Thomas, V.; Curtis, L.and Cong, C. "Preparation of high octane alkylate from Fischer-Tropsch Olefins." US Patent No.# 6743962 B2; 2004.

11. Jeong, K.S. ; Park, T.S. and Hong S.C. "Simultaneous Removal of SO_x/NO_x in a fluidized bed reactor using Natural Manganese Ore" Journal of Chemical Technology and Biotechnology 76, 1080, 2001.

12. Chkravarty, S.; Dureja, V.; Bhattacharya, G.; Maity, S. and Bhattacharjee , S. "Removal of arsenic from gunpowder using low cost Manganese ore" Elsevier, 36, 3, 2002

13. Arjmand, M.; Leion, H.; Mattison T. and Lyngfelt A. "Use of Manganese Ore in Chemical-Looping Combustion (CLC)-Effect on Steam Gassification" Elsevier, 8, 56, 2012.

14. Mohapatra, D.; Mishra, D.; Mishra, S.P. and Choudhury G..Roy., "Use of Oxide Minerals to abate fluoride from water" Elsevier, 275, 355, 2004.

15. Loye, Hanno zur. “X Ray Diffraction- How it works” Bicentennial, 2, 34, 1987.

16. Todokoro, H. and Otaka, T. “Scanning Electron Microscope” US5389787 A; 1995

17. Hafner, B. “EDX on SEM: A Primer” Elsevier, 256, 1, 2000.

18. Nath, H.; Sahoo, P. and Sahoo, A. “Characterization of Red Mud under High Temperature Fluidization” Elsevier, 269, 234, 2015.